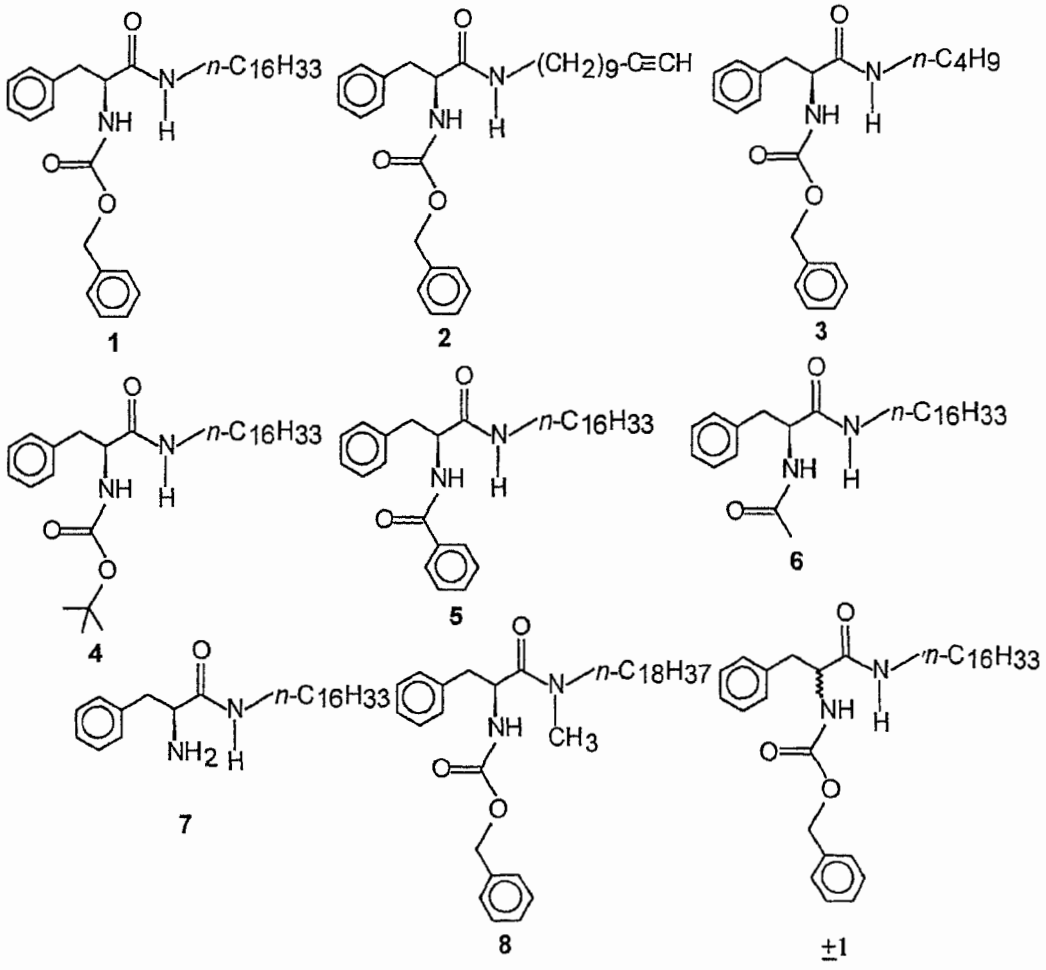
SYNOPSIS

The thesis entitled "Development of New Molecular Materials based on Self-assembly Strategies" describes the self-organization and material properties exhibited by a few supramolecular organizations generated from various molecules designed on the basis of specific structural considerations. The thesis consists of four chapters, the summary of which is given below.

Chapter 1 deals with the gelation and aggregation properties exhibited on self-assembling of *N*-benzyloxycarbonyl-*L*-phenylalanine based amphiphiles and an in-depth study of their structure-property relationship. Synthetic routes leading to twelve *L*-phenylalanine based mono and bipolar derivatives (**1-12**) have been presented. These include monopolar systems such as *N*-Benzyloxycarbonyl-*L*-phenylalanine-*N*-alkylamides and the corresponding bipolar derivatives with flexible and rigid spacers such as with 1,12-diaminododecane and 4,4'-diaminodiphenylmethane respectively. The two ends of the latter have been functionalized with *N*-benzyloxycarbonyl-*L*-phenylalanine units via amide connection. Another bipolar molecule was synthesized in which the middle portion of the hydrocarbon segment contained polymerizable diacetylene unit. To ascertain the role of the presence of urethane linkages in the gelator molecule, protected *L*-phenylalanine derivatives were also synthesized in which the benzyloxycarbonyl group has been replaced with t-butyloxycarbonyl, acetyl and benzoyl groups respectively. Upon completion of the synthesis and adequate characterization of the newly described molecules, we examined the aggregation and gelation properties of each of them in a number of solvents and their mixtures. The systems that formed gels were further characterized by optical microscopy and electron microscopy (Fig. 1). Few representative systems which showed excellent gelation behavior was further examined by FT-IR, calorimetric and powder X-ray diffraction studies. To explain the possible reasons for gelation, the results of molecular modeling and energy minimization studies were also included.



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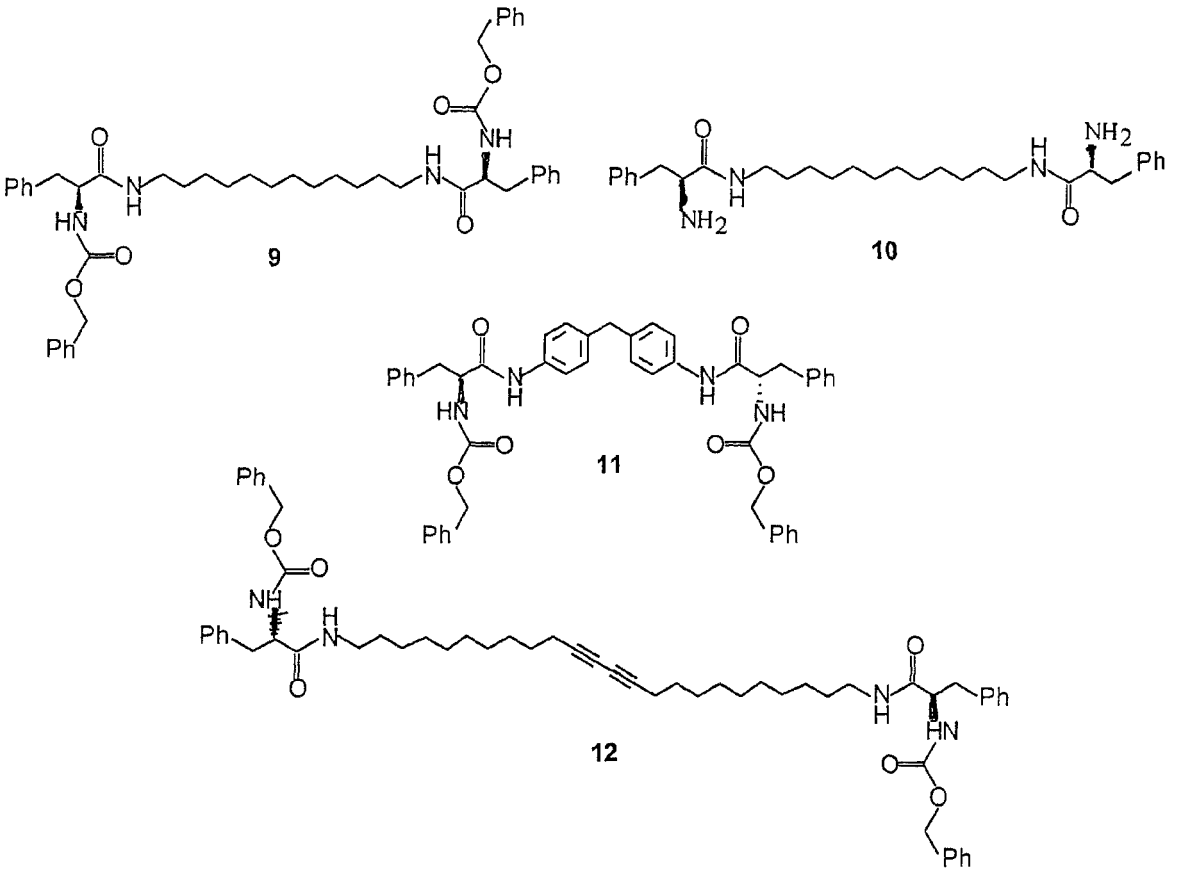
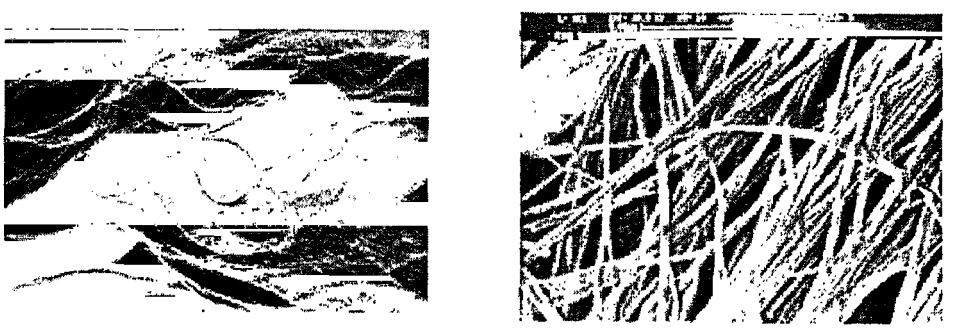


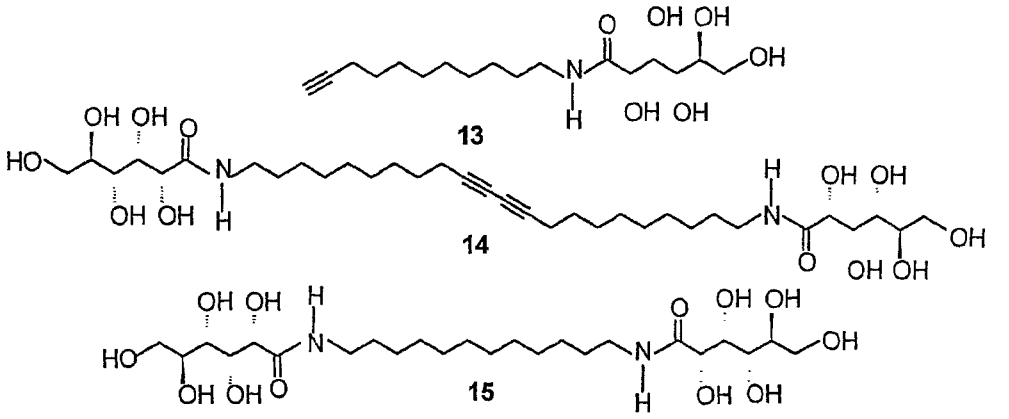


a b

Fig. 1: Micrographs of the gel of **1**, Optical Micrograph (Fig.1a) and SEM (Fig.1b).

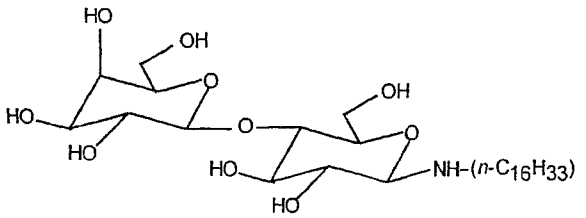
Chapter 2 deals with the synthesis and studies of the aggregation properties of a chiral monopolar amphiphile and two bolaamphiphiles (**13-15**) having *D*-gluconamide as head group. One of the bolaamphiphiles included a diyne unit in the hydrophobic center, which undergoes polymerization in membranous assemblies upon exposure to light. This bolaamphiphile prior to polymerization afforded nanoscopic structures like helical ribbons and fibers at slightly basic pH, but in pure water it generated a thin film. The polymerization of the diyne units in this molecule led to the formation of spherical structures. The resulting aggregate was found to be violet colored. The polymerization of the diyne units in this molecule however, did not take place in basic solution. On the other hand the dispersion of the other bolaamphiphile which did not contain any diyne units in its hydrophobic interior was stable in water solution in hot condition (>70 °C) only and precipitated at ambient temperature. The monopolar amphiphile formed platelets in pure water but in KOH solution, it formed rod- and tape-like microstructures. Monolayer membranes of the diacetylenic

bis-*D*-gluconamide bolaphiles could be readily polymerized in water to afford a violet colored polymer that was sparingly soluble in water. The time-course of this polymer formation and influence of cosolubilization in cationic CTACl micelles have also been examined.



Chapter 3 was divided into two sections. Section **A** deals with the studies related to hydrogel formation from a few synthetic, non-polysaccharide amphiphile systems. Altogether six compounds (**16-21**) were synthesised. Spectroscopic and analytical data obtained for these compounds were consistent with their given structures. Since the gels formed from the above substances showed the ability to 'trap' water molecules upon gelation, these gels were described as 'hydrogels'. When these gels were heated to ~70 °C, the samples turned into clear, isotropic fluids and upon gradual cooling, the hydrogels could be reproduced. Thus these systems were also 'thermo-reversible'. The low molecular mass (MW 565) of the gelators (for **16** and **17**) compared to that of a typical polymeric gelator forming substance implies pronounced aggregation of the disaccharide amphiphiles into larger microstructures during gelation. In order to discern the aggregate textures and morphologies, the specimen hydrogel samples were examined by high resolution scanning electron microscopy (SEM) (Fig. 2). In contrast to their single-chain counterparts, the double-chain lactosyl and maltosylamine amphiphiles upon solubilization in EtOH-H_2O afforded hydrogels, with reduced mechanical strengths. Interestingly, the corresponding microstructures were found to be quite different from the corresponding hydrogels of their single-chain counterparts. Rheological studies provided further insights into the behavior of these hydrogels. To explain the possible reasons of gelation, the results of molecular modeling and energy minimization studies were also included.

Section **B** of Chapter **3** deals with the vesicle formation from some of the above mentioned disaccharide based amphiphiles. Two new sugar based amphiphiles (**22-23**) were also synthesized. Four of these contain one hydrocarbon chain in their hydrophobic segment. The other four compounds have two hydrophobic chains. Electron Microscopy indicated that six of these formed bilayer membranes upon dispersion in aqueous media. Formation of vesicles in the closed aqueous compartments from these amphiphiles was confirmed by dye entrapment studies. X-ray diffraction of the cast films of these amphiphiles was performed to elucidate the nature of packing and the thicknesses of these membranous organizations.



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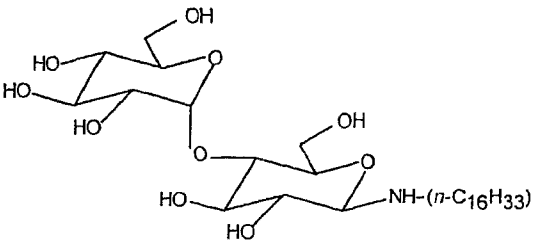

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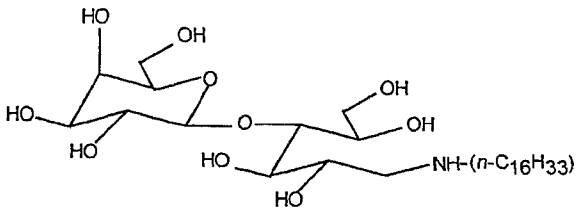

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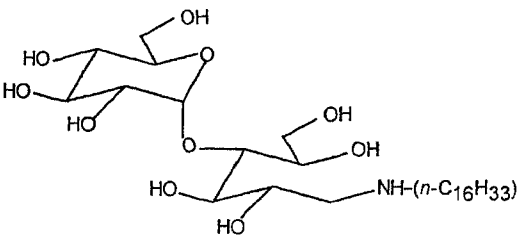

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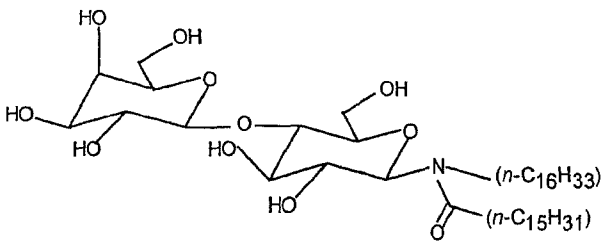

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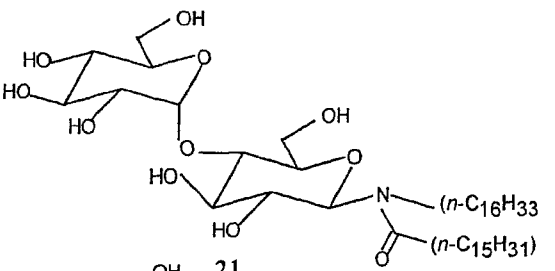

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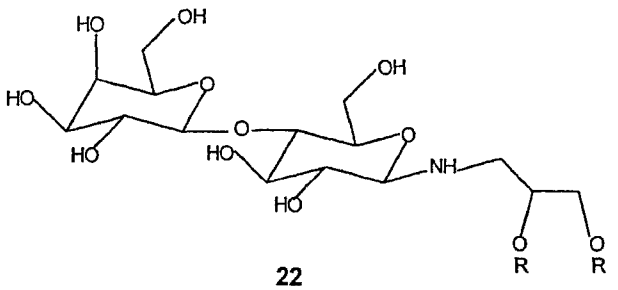

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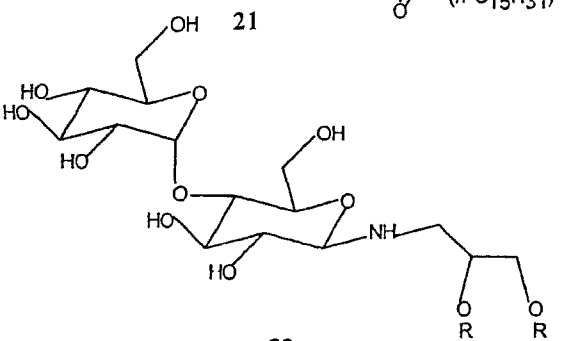
R = n-$C_{16}H_{33}$



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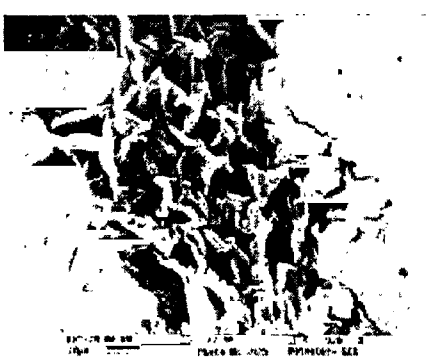

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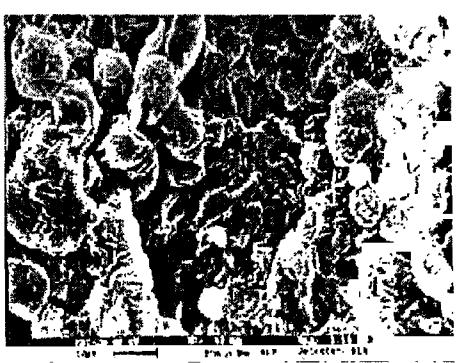

b

Fig. 2: SEM pictures of the hydrogels of **16** (Fig. 2a) and **17** (Fig. 2b).

Chapter 4 describe the design and synthesis of novel self-assembled solid–state structures elucidated on the basis of single-crystal X-ray crystallography. These materials were derived from triazine-2,4,6-*tris*dimethyliminodiacetate, triazine-2,4,6-*tris*iminodiaceticacid, and their corresponding potassium and calcium salts. These molecules incorporated well-defined patterns of supramolecular association through π-stacking, electrostatic and hydrogen-bond donor and acceptor interactions (Fig. 3). From these studies it may be concluded that small variations in the starting scaffold induces significant changes in its solid-state aggregation properties which results in the formation of novel crystalline motifs.

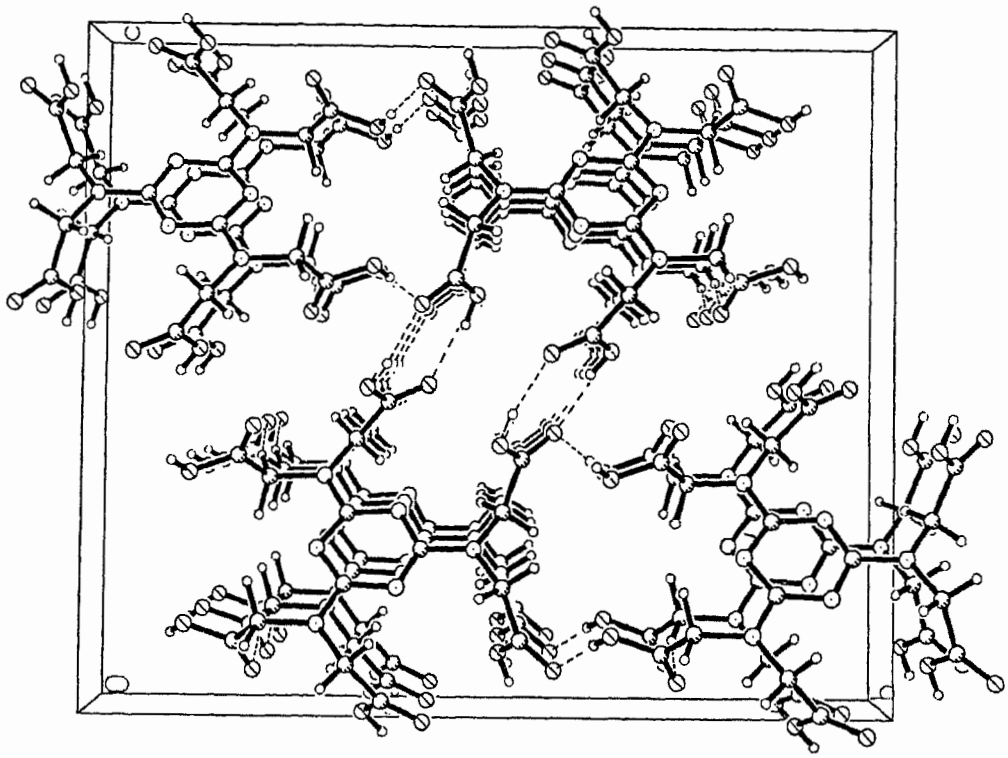

Fig. 3 Packing diagram of the crystalline supramolecular assemblies of triazine-2,4,6-*tris*iminodiaceticacid.